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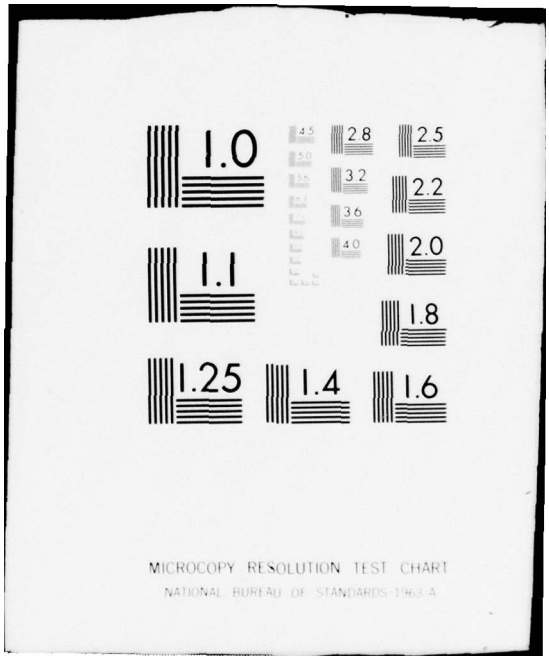
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FJSRL TECHNICAL REPORT - 78- 0008
AUGUST 1978

XENON DIFLUORIDE FLUORINATION. MECHANISM AND SELECTIVITY OF BORON TRIFLUORIDE ETHERATE CATALYSIS IN THE NORBORNENE MODEL

CAPT SCOTT A. SHACKELFORD

PROJECT 2303

AIR FORCE SYSTEMS COMMAND
UNITED STATES AIR FORCE

FJSRL-TR-78-0008

This document was prepared by the Energetic Materials Division, Directorate of Chemical Sciences, Frank J. Seiler Research Laboratory, United States Air Force Academy, Colorado. The research was conducted under Project Work Unit Number 2303-F3-03, Chemistry of Xenon Difluoride. Captain Scott A. Shackelford was the Project Scientist in charge of the work.

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE	READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER: FJSRL-TR--78-0008	2. GOVT ACCESSION NO. (1)
	3. RECIPIENT'S CATALOG NUMBER: Technical Rept.
4. TITLE (and Subtitle): Xenon Difluoride Fluorination. Mechanism and Selectivity of Boron Trifluoride Etherate Catalysis in the Norbornene Model.	5. TYPE OF REPORT & PERIOD COVERED: 18 Aug 75 - 15 Jan 78
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): Capt Scott A. Shackelford	8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Frank J. Seiler Research Laboratory, U.S. Air Force Academy, CO 80840	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS: 2303-F3-03
11. CONTROLLING OFFICE NAME AND ADDRESS	12. REPORT DATE: August 1978
	13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office): 50p.	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Boron Trifluoride Etherate
Xenon Difluoride
Difluoronorbornane
Fluorination
Lithium Tetrafluoroborate

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The boron trifluoride etherate initiated fluorination of norbornene with xenon difluoride in dichloromethane solvent selectively produces the novel 2-endo-5-exo-difluoronorbornane and its analogous 2-endo 5-exo-difluoronorbornane represent approximately half the directly fluorinated reaction products, and the well-known anti- and syn-2,7-difluoronorbornane isomers comprise the remainder. Subsequently the boron trifluoride etherate catalyzes selective isomerization of both 2,7-difluoronorbornanes to produce a nearly exclusive

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yield of the 2-exo-5-exo- and 2-endo-5-exo-difluoronorbornane isomers. A change to diethyl ether solvent yields the normal anti- and syn-2,7-difluoronorbornane isomers as the major difluoride products and quenches the boron trifluoride etherate isomerization. Substitution of lithim tetrafluoroborate for the boron trifluoride etherate in diethyl ether solvent again provides the unique 2,5-difluoronorbornanes as the major difluoride products. The 2,5-difluoronorbornane isomers were unambiguously identified by the direct fluorination of deuterated norbornene. The deuterated norbornene also permitted the initial fluorination mechanism and the selective isomerization pathway in dichloromethane solvent to be studied.

FJSRL-TR-78-0008

XENON DIFLUORIDE FLUORINATION
MECHANISM AND SELECTIVITY OF BORON TRIFLUORIDE ETHERATE CATALYSIS IN THE NORBORNENE MODEL

By

Scott A. Shackelford

TECHNICAL REPORT FJSRL-TR-78-0008

August 1978

Directorate of Chemical Sciences
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PREFACE

This report documents work conducted under Work Unit 2303-F3-03, Chemistry of Xenon Difluoride, between 18 August 1975 and 15 January 1978. Research is continuing in the areas mentioned in this report and will be documented as additional technical reports and journal articles. Captain Robert A. Hildreth provided constructive discussions and technical assistance. Constructive discussions and support were received from Lt Colonel Ben A. Loving, Dr. Melvin L. Druelinger, and Lt Colonel Lowell A. King. Mr. J. Lloyd Pflug provided technical assistance and performed all nmr and mass spectral analyses. Mrs. B. Plonsky typed the report. Mr. Fred C. Kibler provided extensive technical assistance and necessary glassblowing support.

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XENON DIFLUORIDE FLUORINATION. MECHANISM AND SELECTIVITY OF BORON TRIFLUORIDE ETHERATE CATALYSIS IN THE NORBORNENE MODEL

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INTRODUCTION

A previously reported benchtop procedure demonstrated xenon difluoride to be a convenient direct fluorinating reagent for aliphatic alkenes.[2] This convenient procedure employed boron trifluoride etherate to catalytically initiate direct alkene fluorination in a dichloromethane suspension. It required only such standard items as a drybox for storing and weighing the xenon difluoride and a benchtop fumehood in which to conduct the fluorinations using standard chemical glassware. When norbornene was fluorinated by this procedure, an unprecendented high yield synthesis of 2-exo-5-exo-difluoronorbornane 1 and its analogous 2-endo-5-exo-isomer 2 occurred.[3] This result was in distinct contrast with previously reported halogen and interhalogen additions to norbornene that selectively produced the anti- and syn-2,7-dihalonorbornane isomers through an ionic mechanism, or the 2-exo-3-exo- and 2-endo-3-exo-dihalonorbornanes from a radical pathway.[4-10] Two past norbornene fluorinations produced three major products common to each reaction. Fluorination with lead tetraacetate/hydrogen fluoride in a Freon 112 dichloromethane solvent,[9] and a more recent fluorination using difluoroiodobenzenes with a dichloromethane/hydrogen fluoride solvent[10] both afforded the ionically rearranged 2-exo-7-anti-difluoronorbornane 3 and 2-exo-7-syn-difluoronorbornane 4, plus nortricyclyl fluoride 11 as the major products. In both cases the syn-2,7-difluoronorbornane 4 proved to be the

predominant species. A more recent hydrogen fluoride initiated reaction between norbornene and xenon difluoride in dichloromethane solvent provided the nortricycyl fluoride 11 as its major product. The 2,7-, 2,5-, and 2,3-difluoronorbornane isomer sets comprised the six additional isolated products.[11]

The boron trifluoride etherate catalyzed fluorination of norbornene with xenon difluoride represents the first selective synthesis of 2-exo-5-exo-difluoronorbornane 1 and 2-endo-5-exo-difluoronorbornane 2 in high yield.[3] When this reaction was conducted over a 20-20 hour period, the two combined 2,5-isomers represented 93 percent or more of the difluoride products (Table I, 87-91% of the total reaction products). The 2-exo-7-anti-difluoronorbornane 3 is the only other difluoride detected as a minor product.[12] When a portion of this same reaction is quenched after only one hour and fifteen minutes, four initial difluoride products were found (Equation 1). The 2-5-difluoronorbornane isomers 1 and 2 comprised slightly more than one half of the fluorinated reaction products. The 2,7-difluoronorbornanes 3 and 4, commonly the major products in nearly all other norbornene fluorinations, halogenations, and interhalogenations, were identified as the remaining two products.[13] Analysis of the unquenched portion of this reaction after 20-22 hours again revealed 1 and 2 to be nearly exclusive difluoride products (Table I). This result suggested that the 2,7-difluoronorbornane

- INSERT EQUATION 1 -

isomers were selectively isomerized into additional 2,5-difluoronorborane products during the extended 20-22 hour reaction time. This sterospecific

Table I. Difluoronorbornane Isomer Product Distribution From Boron Trifluoride Etherate Catalysis in CH_2Cl_2 Solvent.

Run	Conditions	1	2	3	4	5	6	7	11
1	A	(Combined 98.5)		1.5	0	0	0	D	0
3	A	45	17	38	0	0	0	D	0
4	A	66.5	30	3	0	0	0	D	0
5	A	64	29	7	0	0	0	D	0
6	A (dark)	65	31	4	0	0	0	D	0
7	B[a]	58	26	3	0	0	0	13	0
	C[b]	24.5	26	43	7	0	0	0	0
8	B[c]	62	26	3	0	0	0	9	0
	C[d]	40	17	31	12	0	0	0	0
9	C[e]	22	26	42	9	0	0	0	0
10	(A No Catalyst)	19	28	37	5	0	4	0	8
ref 11	(HF Catalyst)	11	20	19.5	6	2	3.5	0	38

A. -78°C to room temperature, 20-22 hr. B. -46°C to room temperature, 20-22 hr. C. -4°C to -39°C, 1 1/4 hr. D. Not determined.

[a] Product percentages change to 1 (66), 2 (30), and 3 when unknown 7 is not considered.

[b] -43°C to -39°C during XeF_2 consumption.

[c] Product percentages change to 1 (68), 2 (28), and 3 (3) when unknown 7 is not considered.

[d] -46°C during XeF_2 consumption.

[e] -41°C during XeF_2 consumption.

isomerization is initiated by the boron trifluoride etherate; no isomerization results in the absence of this fluorinated Lewis acid under identical reaction conditions (Table I).

This paper describes the employment of deuterium labeling and catalyst/solvent variation to study the mechanism and product selectivity afforded by this boron trifluoride etherate initiated xenon difluoride/norbornene fluorination. Additionally, the deuterium labeling provides an unambiguous chemical identification of the unique 2,5-difluoronorbornane isomers.[11,14] Interesting isomeric product reversals were obtained during the catalyst and solvent variation studies. Such isomeric product reversals could prove significant in correlating reaction condition options with desired product control when using this convenient, direct fluorination procedure.

RESULTS AND DISCUSSION

Deuterium Labeling Study. Depending upon the reaction conditions imposed, direct xenon difluoride fluorination of norbornene by boron trifluoride etherate initiation in a dichloromethane suspension produced either three or four difluoronorbornane compounds 1, 2, 3, and 4. The identity of 3 and 4 proved to be the previously reported 2-exo-7-anti- and 2-exo-7-syn-difluoronorbornane isomers respectively;[9] however, compounds 1 and 2 represented an unreported isomeric pair.[14] The symmetrical pattern displayed by the ^{1}H and ^{19}F nmrs of 1 suggested this new difluoride to be either 2-exo-5-exo-difluoronorbornane or the analogous 2-exo-3-exo-isomer.[15] Compound 2 was presumed to be a cooresponding endo-exo-isomer. Its somewhat similar geminal-HF pmr splitting pattern to that exhibited by the minor 2-endo-5-exo-dibromonorbornane product previously isolated, further

supported this assignment.[16] A dehydrofluorination of 1 yielded a fluoronorbornene which by itself failed to conclusively differentiate between the 2-exo-5-exo-difluoronorbornane or the 2-exo-3-endo-isomer. Spectral characterization to identify 1 and 2 was also inadequate since a comparison of all four potential isomers was not possible from this reaction system. Therefore, deuterium labeling of the norbornene was used to verify the isomeric identity of 1 and 2.

Fluorination of 2-deuterionorbornene was conducted under the same reactions used with unlabelled norbornene. A portion of this reaction was quenched after one hour and fifteen minutes so the initially formed reaction products could be isolated and analyzed. The absence of a proton magnetic resonce (pmr) signal from the deuterium atom incorporated in products 1 and 2 afforded an unambiguous identification between the 2,5-difluoro- and 2,3-difluoronorbane isomeric pairs. A radical fluorination mechanism would produce the unrearranged, deuterated 2-exo-3-exo- and 2-endo-3-exo-difluoronorbornane isomers for 1 and 2 respectively (Equation 2).[5]

- INSERT EQUATION 2 -

These compounds would reveal a geminal-HF pmr signal one-half the integrated value (one proton) of their analogous unlabeled compounds (Table II). Clearly the pmr results outlined in Table II reveal the 2-exo-3-exo and 2-endo-3-exo-difluoronorbornanes are not produced. Instead fractional geminal-HF pmr values appear for both the 1 and 2 isomers (Table II). Such fractional values must be produced from a norbornyl structural arrangement

that is characteristic of an ionic reaction mechanism. Thus, 1 and 2 represent 2-exo-5-exo-difluoronorbornane and 2-endo-5-exo-difluoronorbornane, respectively, which only can form by rearrangement within the norbornyl structural skeleton. The initial formation of both ionically generated 2,7-difluoronorbornane isomers 3 and 4 in addition to 1 and 2, the successful fluorination of a nitrated aliphatic alkene,[2] and the total absence of any 2,3-difluoronorbornanes 5 and 6,[3] all strongly support an exclusive ionic fluorination mechanism. This ionic fluorination's novel selectivity in producing substantial amounts of 1 and 2 was studied further with deuterium labeling.

Additional pmr analysis of all four initial products from the 2-deuterionorbornene/xenon difluoride fluorination provided an excellent method for tracing the progress of this selective ionic reaction and for investigating its resultant preferential isomerization pathway. Scheme 1 represents an ionic mechanism consistent with the rearranged deuterium atom of all four initially formed products 1, 2, 3, and 4. The amount of deuterium rearrangement predicted by scheme 1 is recorded in Table II. Excellent agreement is obtained between that predicted and found from pmr analysis of the initially formed 1, 2, 3, and 4 difluoride products. The slightly low gem-HF and high norbornyl skeleton integration for 1 possibly results from a higher degree of initial fluorination at the deuterium labeled vinyl carbon. An initial 5,3-hydride migration eventually produces both the 2,5-difluoronorbornanes 1 and 2. Alternatively, both 2,7-difluoride isomers 3 and 4 result from an initial sigma bond 4,3-shift (scheme 1).

Table II. Predicted and Actual Initial Product pmr Signals from 2-Deuterionorbornene/XeF_2 Fluorination.

Product	Gem-HF	Bridgehead	Bridge[a]	Norbornyl Skeleton
6 Calc.	1.0	2.0	-	6.0
5 Calc.	1.0	2.0	-	6.0
4 Calc.	1.5	1.5	-	6.0
Actual[b]	1.5	1.5	-	6.0
3 Calc.	1.0	1.5	0.5	6.0
Actual[b]	1.0	1.5	0.5	6.1 (6.06)
2 Calc.	1.5	2.0	-	5.5
Actual[b]	1.5	2.0	-	5.5
1 Calc.	1.5	2.0	-	5.5
Actual[b]	1.4	2.0	-	5.6

[a]Only the 2-exo-7-anti-difluoronorbornane isomer 3 possesses a chemical shift which allows separate evaluation of the bridge proton(s).

[b]Reaction Conditions: -43 to -30°C, 1 1/4 hr., all XeF_2 consumed.

The ionic fluorination mechanism outlined in scheme 1 also reveals three possible factors that contribute to the highly selective production of both 2,5-difluoronorbornane isomers 1 and 2 as compared to other norbornene halogenations. The first factor involves formation of the very stable 9 type carbonium ion species. The fluorinated carbonium ions 9a and 9b that produce the 2-5-difluoronorbornane isomers 1 and 2 respectively, rearrange from the initial 8 species to place the positive charge density the farthest possible distance from the fluorine bonded carbon atom. In the case of the 9 type fluorinated carbonium ion species, the positive charge density is three carbon centers away. The 10 type fluorinated carbonium ion that yields both 2,7-difluoronorbornanes possesses its positive charge closer to the fluorine bearing carbon atom just two centers away. The extremely high electron withdrawing properties of the bonded fluorine atom in 8 must be sufficiently long range to require the additional stablization provided by the 9 type species over the 10 type carbonium ions.[17] Such additional stabilization apparently is not required in norbornene additions with the other less electronegative halogens. A second factor contributing to the high degree of 1 and 2 product formation could be attributed to a favorable steric attack by the fluoride ion. The fluoride ion attack in both 9 species occurs from a direction that minimizes repulsive elctronic interactions between the high electron density of the bonded fluorine atom and the attacking fluoride ion. This same electronic interaction minimization is also found in the 10a species that provides product 3. Interestingly products 1, 2, and 3 constitute ninety percent or more of the initial fluorinated products, while the minor product 4

is generated from species 10a where possible fluorine-fluorine interactions are not minimized. Other norbornene halogenations have often produced the analogous syn-2,7-isomer as the major dihalide product.[4-6,8,9] The third factor involves the role of the boron trifluoride etherate catalyst. All four initial fluorination products are formed from 9 or 10 type rearranged carbonium ion species which are generated from 8 through sigma bond and hydride migrations. Formation of 9 and 10 from the initially produced 8 carbonium ion species results from the energetically unfavorable situation encountered in electrophillic additions when a positive charge resides adjacent to a fluorine bonded carbon atom.[18] A concomittant tetrafluroborate anion formation during the fluorination (scheme 1) could promote the selective rearrangement of 8 to the most stable 9 species by providing the stable boron tetrafluoroborate counter ion. This tetrafluoroborate anion provides a site for the second fluorine atom from XeF_2 to reside during the time required for rearrangement. Naturally the attacking fluoride ion upon species 9 and 10 can be any one of the fluorine atoms comprising the tetrafluoroborate anion and is not necessary the same fluorine originally bonded in the xenon difluoride reactant. Evidence for the tetrafluoroborate anion formation and participation is discussed and verified in the catalyst/solvent variation study outlined herein.

The tetrafluoroborate anion also appears to participate in the selective isomerization of the anti-2,7-difluoronorbornane 3 mostly to 2-exo-5-exo-difluoronorbornane 1 and some to 2-endo-5-exo-difluoronorbornane 2. A review of Table I illustrates that runs 1-6, 7B, and 8B are very consistent

in the percentage of 1, 2, and 3 products initially produced; however, run 3 provided an exception. Since neither varying the concentration of the boron trifluoride etherate catalyst (runs 1, 4, and 5)[26] nor varying the amount of light exposure (runs 5 and 6) significantly altered the isomeric product percentages, an acid catalyzed isomerization of the initially formed products was suspected. Two reactions were conducted where one half of the reaction solution was aliquoted and quenched 1 1/4 hours after the addition and disappearance of the XeF_2 reagent (runs 7C and 8C). The remainder of the reaction solutions were allowed to proceed for a total of 20-22 hours (runs 7B and 8B) under the experimental conditions of runs 1-6. A comparison of run 7B to 7C and of 8B to 8C reveals that all but three to four percent of 3 isomerized mostly to 1 and some to 2. Further verification that boron trifluoride etherate effected the isomerization of 3 to 1 and 2 was achieved by stirring pure anti-2,7-difluoronorbornane 3 in dichloromethane with boron trifluoride etherate under the time and temperature conditions employed in runs 1-6. Analysis of glpc revealed unisomerized 3 (4%), 1 (65%), 2 (29%), and the unidentified isomer 7 with a high glpc retention time.[12] The XeF_2 fluorination of 2-deuterionorbornene (Table II) was conducted under the same experimental conditions of runs 7 and 8 (Table I). By dividing this reaction solution and comparing the initial and isomerized reaction products of 1, the increase or decrease of pmr signals at specific deuterated positions allowed a more detailed study of the isomerization pathway of 3 to 1.

Table III. Proton Magnetic Resonance Analysis of Deuterium Atom Changes in 1 By $BF_3O(CH_2CH_3)_2$ Assisted Isomerization.

Reaction Conditions	Gem-HF	Bridgehead H	Norbornyl Skeletal H
A 1.25 hr (-43 to -39°C)	1.4	2.0	5.6
B 21.25 hr (-43 to r.t.)	1.5	1.9	5.6
Predicted Change (A to B)	increase	decrease	no change

Reaction condition A (Table III) represents the pmr integration of the initially formed 1 isomer listed in Table II and predicted in scheme 1. Reaction condition B displays the change in pmr integration of 1 after isomerization. Isomer 1 was chosen for this comparison since it is the predominant isomer produced in this selective isomerization of species 3. Comparing both 1 isomers initially produced (scheme 1) with the two 1 isomers predicted by the scheme 2 isomerization pathway, reveals that the selective isomerization of 3 to 1 should decrease the pmr signal at the bridgehead position where no deuterium atom initially existed. Additionally the geminal-HF pmr signal should increase by producing two new 1 isomers (scheme 2) with no deuterium atom incorporated at this position, and no change should occur in the pmr signal in the remaining 2-exo-5-exo-difluoronorbornane structural skelton. These changes outlined by scheme 2 agree with those actually found (Table III). Nonselective isomerization of difluoronorbornane isomers in the presence of the Lewis acid hydrogen fluoride has been reported[11] and was attributed to an anologous process which effects an ionic hydrogen fluoride catalyzed hydrolysis of benzyl fluoride.[19] Just

as the Lewis acid hydrogen fluoride apparently seeks out a highly concentrated nonbonded electron pair on the fluorine atom, the vacant p-orbital of the boron atom in the boron trifluoride Lewis acid species could be expected to behave similarly. Formation of the stable tetrafluoroborate anion would provide a stable species to transport the fluoride ion during isomerization, and once again, allows formation of the same stable 9 monofluoronorbornyl cation (scheme 1) which places the positive charge density three carbon atoms from the fluorine bonded carbon. Continual overnight room temperature isomerization through species 9 (scheme 2) promotes the selective ionic isomerization that produces the major 1 isomer under the longer term reaction conditions. The loss of the initially formed isomer 4 could also be attributed to this boron trifluoride etherate initiated isomerization.

Catalysis/Solvent Studies. Boron trifluoride etherate catalysis selectively provides 2-exo-5-exo-difluoronorbornane 1. Comparison of catalyzed reactions 1-9 (Table I) with a blank XeF_2/norbornene fluorination (Reaction 10) shows the greatest amount of isomer 1 is afforded by the selective boron trifluoride etherate assisted isomerization. However the boron trifluoride etherate catalyzed reactions 7C, 8C, and 9C display some increased selectivity of 1 over that exhibited by the noncatalyzed reaction 10. Scheme 1 invokes formation of the boron tetrafluoroborate anion and its subsequent use as a secondary fluorinating species to explain in part the selectivity toward 2,5-difluoronorbornane isomers. To verify the proposed participation of the tetrafluoroborate anion during initial fluorination, a xenon difluoride fluorination of norbornene was catalyzed directly with the tetrafluoroborate anion in the absence of boron trifluoride

etherate. The tetrafluoroborate anion was introduced into the reaction as the lithium salt, and diethyl ether solvent was employed for improved solubility of the lithium tetrafluoroborate catalyst. Table IV reveals that the presence of the tetrafluoroborate anion effects production of the

Table IV. XeF_2/Norbornene Fluorination Product Percentages: Catalyst and Solvent Variation Data[a].

Catalyst	Solvent	1	2	3	4	5	6	11	12[b]
Blank	CH_2Cl_2	19	28	37	5	0	4	8	0
Blank	Diethyl Ether	9	11	48	16	0	3	12	3
$LiBF_4$	Diethyl Ether	27	15	18	7	0	0	17	15[c]
$BF_3O(CH_2CH_3)_2$	Diethyl Ether[e]	14	12	44	21	0	0	7	0[d]
$BF_3O(CH_2CH_3)_2$	Diethyl Ether[f]	16	13	43	19	0	0	6	3

[a]Difference from 100% are due to the unidentified product.[12]

[b]Compound 12 identified as 2-exo-fluoronorbornane.

[c]This reaction additionally gave 1.1% of an unknown compound (See ref. 29).

[d]Less than 1% (0.3%)

[e]-44° to room temp., 11 hr.

[f]-44°C to room temp., 24 hr.

2-exo-5-exo-difluoronorbornane 1 as the major difluoride. The combined 2,5-difluoronorbornanes 1 and 2 predominated over the more common 2,7-difluoronorbornanes 3 and 4. However, absence of the tetrafluoroborate anion in diethyl ether solvent produced product 1 as the minor difluoride, and

the 2,7-difluoronorbornanes 3 and 4 significantly predominated over both 2,5-difluoronorbnanes 1 and 2. This comparative result strongly supports tetrafluoroborate anion formation as being one significant factor in the selective snythesis of the 2-exo-5-exo-difluoronorbornane product 1. It follows further that the tetrafluoroborate anion of the catalytic lithium salt introduces the second fluorine atom into the two types of monofluoronorbornyl cation species 9 and 10 in an analogous manner to that illustrated in scheme 1. The tetrafluoroborate anion continually would be replenished by the xenon difluoride reagent as it simultaneously introduces the first fluorine atom into the norbornene molecule to generate species 8, 9 and 10.

Significant in the diethyl ether solvolyzed xenon difluoride fluorination of norbornene is the drastic product reversal that resulted when the catalytic species was varied or omitted entirely (Table IV). Reaction with the lithium tetrafluoroborate favored production of the 2,5-difluorides 1 and 2; however, the uncatalyzed fluorination effected a large selectivity for the 2,7-difluoride products 3 and 4. Such potential isomeric control in this fluorination procedure is surprising and could be a consequence of at least two factors. A greater solvating power of diethyl ether solvent over dichloromethane toward ionic species would stabilize species 8 and 10 more effectively and render a decreased necessity for species 9 formation. This would permit the observed increase of products 3 and 4 from species 10. The appearance of nortricycyl fluoride 11 as a fluorination product in diethyl ether solvent also supports this effect. The enhanced ionic stabilization provided by diethyl ether toward species 8 triggers the emergence of a competing fluorination - elimination pathway. Equation 3

illustrates a plausible fluorination - elimination pathway that incorporates very well into the common mechanistic process outlined in scheme 1.

- INSERT EQUATION 3 -

Upon formation of species 8, the second fluoride species from XeF_2 may fluorinate the rearranged catonic species 9 and 10 as they form from species 8, or alternatively, the second fluoride species can effect an elimination upon species 8 to form nortricyclyl fluoride 11. Analogous eliminations previously have been reported with xenon difluoride/alkene fluorinations that produce monofluoroalkenes[2] or other halogenated alkenes.[20] The possible formation of trace amounts of hydrogen fluoride from this elimination pathway could also enhance a lack of product selectivity in the diethyl ether solvent. Secondly, the role of the tetrafluoroborate anion is greatly diminished in the diethyl ether solvent unless the tetrafluoroborate anion is directly introduced. Use of boron trifluoride etherate in diethyl ether solvent continues to favor production of the 2,7-difluoride isomers 3 and 4 (Table IV). Boron trifluoride etherate effects little change in the products obtained when compared to the uncatalyzed fluorination in diethyl ether. Apparently the infinitely high concentration of diethyl ether solvent molecules continuously complexes the boron trifluoride molecules and negates any appreciable tetrafluoroborate anion concentration from forming. The lack of any appreciable 3 and 4 product isomerization to products 1 and 2 (Table IV) also illustrates the inability of complexed boron trifluoride to convert to a tetrafluoroborate anion as outlined in scheme 2.

CONCLUSION

The boron trifluoride etherate initiated fluorination of norbornene with the xenon difluoride reagent initially produces four difluoride addition products. Whether dichloromethane or diethyl ether solvent is employed, 2-*exo*-5-*exo*-difluoronorbornane 1, 2-*endo*-5-*exo*-difluoronorbornane 2, 2-*exo*-7-*anti*-difluoronorbornane 3, and 2-*exo*-7-*syn*-difluoronorbornane 4 are the four initial difluoronorbornane isomers obtained; however, an interesting product reversal occurs depending upon which solvent is used. With dichloromethane solvent the two unique 2,5-difluoronorbornane isomers collectively predominate, while the normal 2,7-isomers, produced in other halogenation and interhalogenation additions, are selectively synthesized in diethyl ether. Extended reaction times in dichloromethane solvent affords the 2,5-difluoronorbornanes in nearly exclusive yield through a selective isomerization catalyzed by boron trifluoride etherate.[3] Analogous direct fluorination in dichloromethane without the boron trifluoride etherate resulted in a less selective distribution; however, a slightly higher selectivity for the 2,5-difluoronorbornane formation was still observed.

A boron trifluoride etherate initiated XeF_2 fluorination of 2-deuterionorbornene in a dichloromethane suspension unambiguously established the identity of the unique 2,5-difluoronorbornane isomers through *pmr* integration. This identification effectively complements their identification obtained solely from spectroscopic assignments.[11] Proton magnetic resonance product integrations also provided a detailed elucidation of this convenient direct ionic fluorination reaction (scheme 1). The production of 2,7-difluoronorbornane products through structural rearrangement strongly suggested

a mechanism with ionic character. Additional evidence pointing to an ionic character was obtained in a separate photochemical induced XeF_2 fluorination of norbornene which provided only the 2-exo-3-exo- and 2-endo-3-exo-difluoronorbornanes 5 and 6 as pure difluoronorbornane addition products under reaction conditions designed to proceed through a radical pathway.[21] Further pmr analyses of the extended time reaction products in dichloromethane solvent suggested that the selective isomerization of the 2,7-difluornorbornanes 3 and 4 to the unusual 2,5-difluoronorbornanes 1 and 2 proceeds through Lewis acid catalysis. This catalysis (scheme 2) produces the same stable ionic precusor species 9 necessary for the initial 2,5-difluoronorbornane isomer selectively (scheme 1).

The boron trifluoride etherate performs an important function in the preferential synthesis of the 2-exo-5-exo- and 2-endo-5-exo-difluoronorbornanes in dichloromethane solvent. While it provides some selectivity toward initial 2,5-difluoronorbornane isomer formation, it also initiates the selective isomerization responsible for a nearly exclusive yield of these two 2,5-isomers. In both the initial fluorination (scheme 1) and the selective isomerization (scheme 2) mechanisms, formation of the stable tetrafluoroborate anion represents a key step. The tetrafluoroborate anion provides a stable anion within which the second fluorine atom from XeF_2 can reside while the monofluoronorbornyl cation 8 can rearrange to its most stable species 9. Subsequent secondary fluorination by the tetrafluroroborate anion of the most stable monofluoronorbornyl cation 9 with its charge situated three carbon centers from the fluorine bonded carbon atom, affords the unique 2,5-difluoronorbornanes and regenerates the boron

trifluoride catalyst. Verification of the tetrafluoroborate anion's participation comes from a diethyl ether solvolyzed fluorination which produced the two normal 2,7-difluoronorbornanes as major products. The infinitely high concentration of diethyl ether molecules continually hold boron trifluoride molecule in its etherate complex and no significant tetrafluoroborate anion can form. However, direct introduction of the tetrafluoroborate anion as $LiBF_4$ into the diethyl ether reaction system, in place of the boron trifluoride etherate, produced a dramatic product reversal where the 2,5-difluoronorbornanes collectively predominated over the analogous 2,7-isomers (Table IV). This continual complexation is also responsible for the lack of any significant selective isomerization when using diethyl ether solvent.

Diethyl ether solvent employed in place of dichloromethane provided a large decrease in the formation of both 2,5-difluoronorbornane products. Instead the 2,7-difluoronorbornane compounds greatly predominated over all other reaction products. Interestingly, they represent analogs of the 2,7-dihalonorbornane compounds that are normally formed as the major products in other halogenation and interhalogenation additions. Compared to the dichloromethane solvent, diethyl ether solvolysis offers a higher degree of stabilization to the monofluoronorbornyl cation species 8 and 10 (scheme 1) and sufficiently diminishes the necessity of the stable species 9 formation by the competing hydride-5,3-migration pathway. The formation of nortricyclyl fluoride 11 from species 8 in diethyl ether solvent, but not with dichloromethane solvent, provides additional evidence to this effect. The dichloromethane solvent enhances the 2,5-difluoronorbornane selectivity

in the XeF_2 fluorination of norbornene by maximizing the long range electron withdrawing destabilization effects of the fluorine atom upon the intermediate monofluoronorbornyl cation species. This effect promotes the competing reactant pathway that enhances formation of the most stable monofluronorbornyl cation species 9 (scheme 1). Subsequent fluorination of species 9 affords the unique 2,5-difluoronorbornanes in high yield. The inability of other less electronegative halogens in norbornene halogenations to produce a substantial proportion of 2,5-dihalonorbornanes is taken as additional evidence for operation of long range fluorine effects in dichloromethane solvated XeF_2 fluorination of norbornene. This same factor must also cause the formation of this same stable intermediate species 9 which is necessarily generated during the highly selective isomerization of the 2,7-difluoronorbornanes into their 2,5-isomeric analogs (scheme 2).

The elucidated boron trifluoride etherate initiated ionic fluorination mechanism plus the catalyst and solvent effects upon this direct fluorination procedure, begin to outline the key chemical considerations necessary in predicting and planning future synthetic efforts. The ionic fluorination mechanism, and its propensity to effect the rearrangement of initially formed monofluoronorbornyl ions to more stable forms, can be extended to explain the different major products observed when 1,2-dibromoethene and 1-decene each were fluorinated with the XeF_2 reagent.[2] The demonstrated ability to reverse and control the formation of major difluoronorbornane products through solvent or chemical catalyst variation also defines several important parameters within which selective fluorinations might be obtained. Correlation and integration of these catalyst and solvent

variations within this ionic fluorination mechanism provides an intriguing perspective within which to predict and maximize the reaction conditions necessary for improved, high yield, selective syntheses of novel and important fluoroorganic compounds.

EXPERIMENTAL SECTION

General. In all cases the detailed reaction procedures described herein under "Method A" were followed while conducting the fluorinations. Specifically this applies to the storing, weighing, and transferring of the solid XeF_2 and to the addition method used to introduce the norbornene, catalyst, and solvent into the reaction system.

The acetone used to rinse and dry all items for this direct fluorination procedure was Burdick and Jackson "Distilled in Glass" and was used as received. The water employed in all operations was taken directly from the laboratory's distilled water line. The dichloromethane solvent was Matheson, Coleman and Bell Spectroquality. Prior to use it was distilled over NaOH pellets and stored over 4A molecular seives in a Fischer Scientific Company Isolator/Lab drybox (Ser. No. 282) with a modified drying train. The drybox provided a dry N_2 atmosphere under which the solid XeF_2 reagent was also stored in a teflon screw top bottle. The diethyl ether solvent was Mallinkrodt AR. Immediately prior to use, it was refluxed over Na metal until a trace amount of benzophenone indicator turned blue to signify dryness. The boron trifluoride etherate catalyst (Eastman Organic Chemicals, Practical Grade) was vacuum distilled to a pure colorless liquid;[22] it was redistilled whenever discoloration appeared during storage. The $LiBF_4$ (PCR, Inc.) was used as received, but the norbornene (Aldrich Chemical Company) was fractionally distilled to a waxy colorless solid prior to use. The XeF_2 displayed 100% purity in mass spectral analysis on an instrument possessing a 99.9% detection limit. Care must be taken to use only pure XeF_2 in the procedure described. Samples

of XeF_2 that are contaminated with trace amounts of XeF_4 will be explosive if the XeF_4 contaminant air hydrolyzes to XeO_3.[2]

All glassware, capillary pipets, teflon coated magnetic stir bars, and teflon coated spatulas[23] were cleaned by a similar technique to that previously described.[24] The items were soaked in a seven liter stainless steel beaker charged with distilled water and a small amount of Alconox soap. The solution was heated to a mild boil; then, the items were individually removed with tongs and immediately rinsed in succession with distilled H_2O, acetone, distilled H_2O, and acetone. After atmosphere drying, the 35 ml single-necked round bottom flask, teflon coated magnetic stir bar, 14/20 ground glass stopper, spatula (for weighing out the XeF_2), and the graduated cylinder (for measuring out the reaction solvent) were all placed into the Fischer Isolator/Lab drybox to stand overnight. The remaining glassware and equipment remained exposed to the atmosphere on a clean absorbant paper drain pad until needed.

Melting points were obtained in sealed glass capillaries with a Mel-Temp melting point apparatus and are uncorrected. Mass spectra were obtained on either a Hewlett Packard 5990A GC/MS spectrometer equipped with a 5992A GC/MS terminal system or on a DuPont 21-491 dual beam mass spectrometer. With the latter instrument, the product volatility required direct injection using methanol (M+ = 32) solvent. Nuclear magnetic resonance (^1H and ^{19}F) analyses were accomplished with a Varian T-60 spectrometer in $DCCl_3$ solvent. The ^1H nmr spectra were always referenced to TMS. A Varian Aerograph Moduline Series 2700 dual column chromatograph was used to separate, isolate, and identify the fluorinated products using a 10 ft. by

1/4 in. 10% Carbowax 20M on 80/100 mesh Chromasorb W column with a variable column temperature range from 95°C to 195°C. All products isolated from this glpc column were condensed in small glass traps (constructed in this laboratory) that were submerged in a liquid N_2 bath. Isomer product percentages were determined from disk recorder integration scans. There were some unresolvable tars formed in the fluorination reaction which came off the column at fairly high retention times. However, the percent of all isolated products contained in Table I and IV represent 86 to 94% of the total fluorinated products in the boron trifluride etherate catalyzed CH_2Cl_2 solvated reactions (95% uncatalyzed), 87 to 92% in the boron trifluoride etherate catalyzed diethyl ether solvated reaction (63% uncatalyzed), and 83% in the $LiBF_4$ catalyzed diethyl ether solvolyzed fluorination. All elemental analyses were accomplished by Gailbreth Laboratories, Knoxville, TN.

Direct Fluorination of Norbornene with Xenon Difluoride in CH_2Cl_2 Solvent. (Method A). Inside an isolator drybox under a dry N_2 atmosphere, a 35 ml 14/20 single-necked round bottom flask was charged with a teflon coated magnetic stir bar and 0.35 g (2.07) mmol) XeF_2. A small powder funnel with a 14/20 ground glass joint was used to help transfer the XeF_2 with a spatula into 35 ml reaction flask. The 35 ml flask was then immediately stoppered with a 14/20 ground glass stopper. (Note: Neither the flask nor the stopper were treated with any silicone vacuum grease.) Next the spatula and funnel, used to transfer the XeF_2, were rinsed with CH_2Cl_2 at room temperature to destroy any residual XeF_2.[25] Seven ml of the treated CH_2Cl_2 solvent was poured into a 50 ml graduated cylinder, and the drybox

was then purged three successive times with fresh N_2. The spent N_2 was pumped directly into a fume hood exhaust. Next, the stoppered 35 ml reaction flask and the CH_2Cl_2 containing graduated cyclinder were removed from the drybox, hand-carried to a benchtop fume hood, and were placed into the hood. The 35 ml reaction flask was submerged into a dry ice/acetone coding bath (ca. -78°C) to reduce the vapor pressure of the XeF_2 prior to the ground glass stopper removal. Within 15 sec the stopper was removed and was immediately replaced with a 15 ml pressure equalized addition funnel fitted with a Dreirite containing drying tube. This apparatus was assembled prior to the XeF_2 weighing in the drybox. All joints in this apparatus assembly were sealed with silicone vacuum grease including the male joint of the 15 ml addition funnel. The entire apparatus was placed into the 35 ml reaction flask as one unit. Next, 0.18 g (2.14 mmol) norbornene was weighed into 2 ml of the treated CH_2Cl_2 solvent; then, the solution was transferred with a rubber bulb fitted capillary pipet into the 15 ml addition funnel. The drying tube was removed from the addition funnel during this transfer and was then immediately replaced. The norbornene solution was added dropwise to the solid XeF_2 over a 5-10 min period, and the resulting heterogenous suspension was stirred as soon as mechanically possible. A small amount of pure CH_2Cl_2 (ca. 0.5 ml) was used to rinse the inside of the additional funnel; this was also added to the reaction suspension at the same rate. Subsequently 0.10 g (0.17 mmol) boron trifluoride etherate[26] was weighed into 2 ml treated CH_2Cl_2 solvent; then, this solution was transferred in like manner into the 15 ml addition funnel. Within 5-10 min after the norbornene solution addition, the BF_3OET_2

solution was added dropwise to the stirred norbornene/XeF_2 suspension. Again a small amount (ca. 0.5 ml) of pure CH_2Cl_2 was used to rinse the inner walls of the addition funnel, and this wash was allowed to drop into the reaction suspension. The reaction was stirred at -78°C for 5.5 to 6.5 hr; the reaction was extremely slow. The dry ice/acetone cooling bath then was packed once more and insulated with wrapped towels. Over the following 15-16 hours, the bath was allowed to warm to room temperature, and all solid XeF_2 disappeared leaving a dark brown solution. A 30 ml separatory funnel was charged with 10 ml distilled H_2O and 0.25 g NaF to tie up any possible HF formed. The reaction solution was then transferred into the separatory funnel. The 35 ml reaction flask was rinsed with 2 ml CH_2Cl_2, and this rinse was added to the separatory funnel. The CH_2Cl_2 solution was washed with the aqueous NaF solution and separated. The aqueous wash was then extracted with 2 ml CH_2Cl_2, and this was combined with the first CH_2Cl_2 portion. The combined CH_2Cl_2 portions were dried over anydrous $MgSO_4$ and filtered to provide a golden solution. In several cases in vacuo solvent removal was accomplished and afforded 0.10 to 0.18 g of a dark brown waxy solid product mixture. Usually, the CH_2Cl_2 solvent was not removed, and the solution was introduced directly to glpc separation and purification. Analysis with the Carbowax 20M column afforded products 1, 2, 3, and 7. They were isolated from the glpc column in the following order: 2-exo-7-anti-difluoronorbornane 3, volatile white solid (mp 109.5 - 111.5°C, lit. 109 - 111°C); ^1H nmr ($DCCl_3$) δ 5.12 (doublet of broadened singlets, J_d = 58 cps, 1H), 4.58 (doublet of multiplets, J_d = 58 cps, 1H), 2.46 (doublet of multiplets, J_d = 12 cps, 2H), 2.20-0.90 (multiplets, 6H); ^{19}F nmr

($DCCl_3$) + 50.8 ppm from C_6F_6 or + 163.6 ppm from $CFCl_3$ (doublet of multiplets, J_d = 58.7 cps); mass spectrum M^+ 132 (base peak 81); Elem. Anal. Calcd. for $C_7H_{10}F_2$; C, 63.6; H, 7.64; F, 28.7. Found: C, 63.8; H, 7.44; F, 28.8; 2-endo-5-exo-difluoronorbornane 2, volatile white solid (mp 105.0 - 107.0°C); ^1H nmr[16] ($DCCl_3$) δ 4.94 (doublet of multiplets, J_d = 56 cps, 1H), 4.80 (doublet of broadened doublets, J_d = 56 cps, 1H), 2.62 (multiplet, 2H), 2.30-0.60 (multiplets, 6H); ^{19}F nmr ($DCCl_3$) + 30.6 ppm from C_6F_6 (doublet of multiplets, J = 58.6 cps); mass spectrum M^+ 132 (base peak either 85 or 86); Elem. Anal. Calcd. for $C_7H_{10}F_2$; C, 63.6; H, 7.64. Found: C, 61.8; H, 7.32; 2-exo-5-exo-difluoronorbornane 1, volatile white solid (mp 106.0 - 107.2°C); ^1H nmr[15] ($DCCl_3$) δ 4.48 (doublet of multiplets, J = 56 cps, 2H); 2.46 (multiplet, 2H), 2.20 - 1.10 (multiplets, 6H); ^{19}F nmr ($DCCl_3$) + 3.0 ppm from C_6F_6 (multiplet resembling a quintet); mass spectrum M^+ 132 (base peak either 85 or 86); Elem. Anal. Calcd. for $C_7H_{10}F_2$; C, 63.6, H, 7.64; F, 28.7. Found: C, 63.3; H, 7.45; F, 29.1; product 7[12].

(Method B). All procedures outlined in Method A were repeated with two exceptions. A chlorobenzene/dry ice cooling bath (ca. -43°C) was used in place of the acetone/dry ice bath; and secondly, one half of the reaction solution was removed early, quenched and analyzed. The remainder of the reaction solution was allowed to proceed as in Method A. Depending upon the amount of dry ice used, the temperatures in the chlorobenzene/dry ice bath varied from -46°C to -41°C. In one case (Table I), a reaction at -43°C gradually warmed to -39°C during the 15-20 minutes that the XeF_2 was consumed; two other reactions were held at -41°C and -46°C during consumption of the XeF_2. One hour and fifteen minutes after the addition of the

BF_3OEt_2 solution was first added, approximately one half of the reaction solution (ca. 3 ml) was removed and placed into 10 ml aqueous NaF solution. The quenched aliquoit was worked up and glpc analyzed. Four products were isolated off the Carbowax 20M in the following order: 3, 2, 1, and 4. 2-exo-7-syn-difluoronorbornane 4, volatile white solid; ^1H nmr ($DCCl_3$) δ 4.80 (doublet of broadened singlets with shoulders, J_d = 56 cps, 2H), 2.46 (doublet of multiplets, J_d = 12 cps, 2H), 2.12 - 0.66 (multiplets, 6H); mass spectrum M^+ 132 (base peak 81).[11] Note: Method B was used in the XeF_2 fluorination of the 2-deuterionorbornene sample.

(No BF_3OEt_2 Catalysis). All procedures outlined in Method A were followed identically with one exception. No boron trifluoride etherate catalyst was added. Instead a 2 ml blank of pure CH_2Cl_2 solvent was added to the stirred norbornene/XeF_2 reaction suspension in place of the BF_3OEt_2/CH_2Cl_2 2 ml solution. At the end of the reaction period, the homogeneous reaction solution was a clear gold. Analysis with the Carbowax 20M glpc column afforded six products in the following order: 11, 6, 3, 2, 1, and 4. 2-nortricyclyl fluoride 11, very volatile white solid; ^1H nmr ($DCCl_3$) δ 4.68 (doublet of broadened singlets, J_d = 60 cps, 1H), 1.98 (doublet of broadened singlets, J_d = 12 cps, 2H), 1.28 (broadened singlet, 7H); mass spectrum M^+ 112 (base peak 97); 2-endo-3-exo-difluoronorbornane 6, volatile white solid; mass spectrum M^+ 132 (base peak 67 with 68 as 82%); glpc retention time on Carbowax 20M column identical to major product of a photochemical initiated XeF_2/norbornene fluorination[21] which was identified as 2-endo-3-exo-difluoro-norbornane by ^1H nmr and mass spectrum analysis.

Direct Fluorination of Norbornene with Xenon Difluoride in Diethyl Ether Solvent. Initial preparations and procedures were conducted identically with those outlined for Method A in the CH_2Cl_2 solvolyzed reactions except that diethyl ether solvent was used in place of CH_2Cl_2.

(Boron Trifluoride Etherate Catalysis). A 35 ml single-necked round bottom flask, containing a teflon coated magnetic stir bar, was charged with 0.35 g (2.07 mmol) XeF_2. The XeF_2 containing reaction flask was submerged into a chlorobenzene/dry ice cooling bath (-44°C), and the final reaction apparatus was assembled as previously described (Method A). Next, 0.23 g (2.44 mmol) norbornene was weighed into 2 ml Et_2O, and this solution was added dropwise over 4 min to the XeF_2 containing reaction flask. Stirring was begun as soon as mechanically possible. Nine minutes after addition of the norbornene ethereal solution, 0.1 g BF_3OEt_2 was weighed into 2 ml Et_2O, and this solution was added dropwise over 5 min to the stirred reaction suspension. After 2.33 hr, a reaction aliquot was analyzed by glpc/ms, and no difluoride products were found. A CCl_4/dry ice bath, and a homogeneous then substituted for colder chlorobenzene/dry ice bath, and a homogeneous solution gradually resulted. Some fluorinated products were found after 4.75 hr reaction time. After 6.66 hr, 1 ml additional Et_2O was added to the reaction solution to replenish some volatile solvent loss. After 10.5 hr the cold bath had warmed to -5°C, and the bath was removed. At 11.0 hr half the reaction (ca. 2 ml) was removed for work up and analysis. The CCl_4/dry ice cold bath was again placed around the reaction flask, then was repacked with dry ice and insultated with towels. Again 1 ml Et_2O was added

to the reaction to replenish evaporated solvent, and the remaining solution was left to react further. Meanwhile the aliquoted solution was washed with 10 ml distilled H_2O containing 0.22 g NaF, 0.20 g KI, and 2 capillary pipet drops of 2N H_2SO_4.[27] The ethereal layer was separated, and 1.5 ml of fresh Et_2O was used to extract the aqueous solution. The two ethereal portions were combined, dried over anhydrous $MgSO_4$, and were filtered. The nearly colorless (slightly yellow) solution was analyzed by glpc, and the products eluted from the Carbowax 20M column in the following order: 11, 3, 2, 1, and 4.

(No Boron Trifluoride Etherate Catalysis). All reaction preparations and procedures were conducted in a similar manner to that discussed in the analogous BF_3OEt_2 catalyzed reaction; however, this uncatalyzed reaction proceeded much more slowly. The 35 ml single-necked round bottom flask was charged with a teflon coated magnetic stir bar and 0.35 g (2.07 mmol) XeF_2. After cooling this reaction flask in an acetone/dry ice bath, a 2 ml Et_2O solution containing 0.20 g (2.13 mmol) norbornene was added dropwise to the XeF_2 containing reaction flask over a 5 min period. Stirring was initiated as soon as mechanically possible. Seven minutes after addition of the norbornene solution, 2 ml Et_2O was added dropwise to the stirred reaction suspension over a 3 min duration. After 4.75 min solid XeF_2 remained in a colorless solution. The acetone/dry ice bath was repacked, insulated with towels, and was permitted to warm to room temperature over the next 16 hr. At this point the reaction was recooled in an acetone/dry ice bath, and a white solid formed on the flask's inner wall just above the solution. The

cold bath was removed, and 1 ml Et_2O was added dropwise over 1.5 min to cover the solid formed on the inner wall. All solid dissolved as the colorless reaction solution returned to room temperature. At 28.5 hr the reaction solution began to turn yellow. After 44 hr the reaction was dark brown, and at the 46.5 hr point, the reaction solution was worked up and glpc analyzed as described in the analogous BF_3OEt_2 catalyzed reaction. The reaction products were isolated from the Carbowax 20M glpc column in the following order: 12, 11, 6, 3, 2, 1, and 4; 2-fluoronorbornane 12, very volatile white solid; ^1H nmr ($DCCl_3$) δ 4.62 (doublet of sharp multiplets, J_d = 57 cps, 1H); 2.44 (doublet of multiplets, J_d = 11 cps, 2H); 2.06-0.80 (multiplet, 8H)[28]; mass spectrum M^+ 114 (base peak 68).

(Lithium Tetrafluoroborate Catalysis). All reaction preparations and procedures were conducted in similar manner to that already described. A 35 ml single-necked round bottom containing a teflon coated magnetic stir bar was charged with 0.35 g (2.07 mmol) XeF_2 and was then placed into a a chlorobenzene/dry ice (-44°C) cooling bath. Next, 0.20 g (2.13 mmol) norbornene was weighed into 4 ml Et_2O. The norbornene solution was added dropwise to the XeF_2 containing reaction flask over a 9 min period, and stirring was begun as soon as mechanically possible. Within 4.5 min after addition all the norbornene solution, 0.20 g $LiBF_4$ solid was added directly to the stirred reaction suspension with the aid of a 30 ml powder funnel that possessed a 14/20 male ground glass joint. After 7.5 hr solid XeF_2 was still present in the reaction suspension. The chlorobenzene/dry ice cold bath was repacked, insulated, and was left to warm to room temperature. After 23 hr, the dark brown reaction solution was poured into 10 ml distilled

H_2O that contained 0.4 g NaF. The ethereal layer was washed and separated. An additional 5 ml H_2O was added to the aqueous wash, and the aqueous wash was then extracted with 2 ml fresh Et_2O. The two Et_2O portions were combined, dried over anhydrous $MgSO_4$, filtered, and were analyzed by glpc. Seven products were separated and isolated from the Carbowax 20M glpc column in the following order: 12, 11, unk[29], 3, 2, 1, and 4.

Dehydrofluorination of 2-Exo-5-Exo-Difluoronorbornane. Using a previously reported dehydrofluorination procedure that provided 7-anti-fluoronorbornene from 3 and 7-syn-fluoronorbornene from 4 respectively[9], 5-exo-fluoronorbornene was synthesized from 2-exo-5-exo-difluoronorbornane 1. The dry DMSO solvent was prepared by refluxing it 2 hr over CaH_2 and then vacuum distilling the DMSO at 29-30°C/0.04 mm onto 3A molecular seives. Under a dry N_2 atmosphere a 10 ml single-necked round bottom flask was charged with a teflon coated magnetic stir bar, 3 ml DMSO, 0.103 g (0.777 mmol) 2-exo-5-exo-difluoronorbornane, and 0.106 g (0.946 mmol) potassium t-butoxide. While still under an N_2 atmosphere, the reaction flask was fitted with a water-cooled reflux condenser topped with a Dreirite containing drying tube. The reaction solution was heated between 95-107°C a total of 17 hours; prior to the last 7 hr of heating, an additional 1 ml DMSO was added to the reaction flask under a stream of dry N_2. After cooling to room temperature, 10 ml H_2O was added to the reaction, and the aqueous DMSO reaction solution was continuously extracted 9 hr with 10 ml CH_2Cl_2. The aqueous DMSO layer was then discarded, and CH_2Cl_2 extract was washed with 8 ml H_2O. This H_2O layer was separated, and then was continuously extracted 3 hr with a few

ml (minimum amount needed to form an organic layer, ca. 2 ml) of fresh CH_2Cl_2. This CH_2Cl_2 portion was separated and combined with the first CH_2Cl_2 extract, and the combined CH_2Cl_2 extracts were washed with another 8ml portion of H_2O. This H_2O wash was then continuously extracted 3 hr with a few ml of fresh CH_2Cl_2 as before. This third CH_2Cl_2 extract was combined with the previous CH_2Cl_2 extracts. These combined CH_2Cl_2 portions were washed with 7 ml fresh H_2O. Again a few ml fresh CH_2Cl_2 was used to extract this 7 ml H_2O wash as before and this fourth CH_2Cl extract was combined with the other CH_2Cl_2 extracts. The combined CH_2Cl_2 extracts were dried overy anhydrous $MgSO_4$, filtered, and were concentrated by careful fractional distillation through a Vigreaux column to about 1.5 ml. Analysis by glpc with the Carbowax 20M column provided three peaks using a 85°C column temperature for 5 min after the air peak followed by a 195°C column temperature for a total of 26 min. The first peak proved to be the volatile 5-exo-fluoronorbornene while the second peak was unreacted 1. The third peak was DMSO. The glpc analysis revealed that 42% of 1 was converted to the dehydrofluorinated product. The 5-exo-difluoronorbornene was isolated off the glpc column using a liquid N_2 bath; it was a volatile white solid; ^1H nmr ($DCCl_3$) δ 6.32 (multiplet, 1H); 5.88 (multiplet, 1H); 4.72 (doublet of multiplets, J_d = 58 cps, 1H); 2.96 (unsymmetrical multiplet, 2H); 1.94 - 1.02 (multiplets, 4H); mass spectrum M^+ 112 (37%) with M/e = 97(53), 86(66), 84(100), 73(84), and 66(82).

Synthesis of 2-Deuterionorbornene.[30] A 100 ml three-necked round bottom flask was charged with 22.1 g (0.384 mol) of one micron 40% Na dispersion (Gray Chemical, Inc.) in petroleum and mineral oil. The flask

was fitted with an N_2 stopcocked inlet and identical outlet, plus an overhead mounted mechanical stirrer apparatus. Next, 20 ml "Distilled-in-Glass" hexane treated with neutral alumina (pH = 6.3) was added to the reaction flask. The flask was submerged into a CCl_4/dry ice cooling bath (-23°C) and cooled with vigorous stirring. This cooled suspension was stirred at high speed while 12.0 g (0.130 mol) n-chlorobutane in 10 ml hexane was added dropwise over 1.3 hr. The n-chlorobutane was dried over 4A molecular seives and passed through neutral alumina (pH = 6.3) prior to its combination with the hexane solvent and introduction into the sodium suspension. After all n-butylchloride was added, the CCl_4/dry ice cooling bath was replaced with an ice bath for 35 min. Next, the CCl_4/dry ice bath was again placed around the reaction flask, and 8 min. later 12.0 g (0.128 mol) norbornene in 15 ml hexane was added dropwise to the stirred reaction suspension over 10 min. The cooling bath was removed and the reaction solution was stirred at ambient temperature for 22.5 hr. The CCl_4/dry ice bath was then placed around the reaction flask for 10 min. and the system was opened to the atmosphere. Next 8.9 g 98% D_2O was very cautiously added dropwise to the rapidly stirred suspension using a disposable capillary pipet. The reaction exothermed slightly after the first few drops of D_2O were added, but all material was contained in the reaction flask. After all the D_2O was added, the cooling bath was removed, and the reaction was stirred at ambient temperature 4.5 hr. The reaction solution was transferred into a separatory funnel; then 75 ml H_2O and 10 ml hexane were also placed into the funnel. The distinct organic layer was separated, and the remaining emulsion was extracted six times with three 20 ml hexane portions

followed by three 40 ml diethyl ether portions. All hexane and ethereal extracts were combined and dried over anhydrous $MgSO_4$. After filtration, the solvent was removed by fractional distillation. The undistilled portion was then distilled through a microwave short path apparatus, and only the material that condensed in the water cooled condenser was retained. Proton nmr analysis revealed this material to be 2-deuterionorbornene. An attempt to further deuterate this 1.9 g sample met with failure; however, the 2-deuterionorbornene sample (0.7 g) was recovered by short path distillation. This sample afforded the following nmr analysis: ^1H nmr ($DCCl_3$) δ 6.04 (sharp multiplet, 1H); 2.86 (sharp multiplet, 2H); 1.86 - 0.66 (multiplets 6H); mass spectrum M+1 = 96 (5.6), M^+ = 95 (12.7), M-1 = 94 (7.5) with m/e = 68 (43.0), 67 (100), and 66 (56.5).

ACKNOWLEDGMENTS. Dr. R.A. Hildreth provided constructive discussions and technical assistance. Constructive discussions and support were received from Dr. B.A. Loving, Dr. M.L. Druelinger, and Dr. L.A. King. Mr. J.L. Pflug provided technical assistance and performed all nmr and mass spectrum analyses. Mrs. B. Plonsky typed the manuscript. Mr. F.C. Kibler provided extensive technical assistance and necessary glassblowing support.

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12. Under these extended 20-22 hr. reaction conditions, an unidentified compound 7 was isolated which comprised only 9-13% of the total reaction products. Its mass spectrum afforded M^+ = 110 (base peak = 67), and its pmr gave no gem-HF signal. This unknown's retention time was greater than 1, 2, or 3.

13. Additional investigation after reference 3 revealed that the 2-exo-7-syn-difluoronorbornane 4 initially forms a minor product (7-12%) but disappears under the extended 20-22 hr. reaction conditions.

14. Subsequent to completing the deuterium labeling study described herein and in reference 3, Zupan, Gregorcic, and Pollak reported the spectroscopic characterization of both 2,5-difluoronorbornane isomers 1 and 2. Both the spectroscopic characterization (reference 11) and this complementary deuterium labeling study agree.

15. A pictorial ^1H nmr of compound 1 is presented in reference 3.

16. Pictorial ^1H nmrs of compound 2 and of 2-endo-5-exo-dibromonorbornane are presented in references 3 and 8 respectively.

17. An example of another long range influence involving this fluorine atom, which covers more than two atomic centers, can be seen in the pmr spectrum of 5-fluoronorborn-2-ene where the two vicinyl protons differ in chemical shift by 24 cps.

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23. Initially only teflon coated stainless steel spatulas were used to handle, transfer, and weigh out the XeF_2 reagent. Later it was found that ordinary clean, dry stainless steel spatulas were satisfactory.

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25. At room temperature a 0.35 g XeF_2 sample reacted with pure CH_2Cl_2 within 5 min. and was totally consumed within 10 min. S.A. Shackelford, unpublished results.

26. In runs 3, 5, and 6 (Table I) 0.20 g (1.41 mmol) BF_3OEt_2 was employed. Runs 1 and 4 contained 0.10 g (0.71 mmol) BF_3OEt_2.

27. The acidified KI was employed as a protective measure should any XeO_3 form from an undetected contaminant in XeF_2. Acidic KI converts XeO_3 immediately to Xe and O_2.

28. This ^1H nmr identical to a previously published ^1H nmr of 2-fluoronorbornane, P.R. Schleyer, W.E. Watts, M.B. Comisarow, R.C. Ford, Jr., and G.A. Olah, J. Am. Chem. Soc., 86, 5679 (1964).

29. This unknown trace product afforded a mass spectrum with M^+ 112 (base peak 84). This mass spectrum is similar to that obtained for 5-fluoronorbornene.

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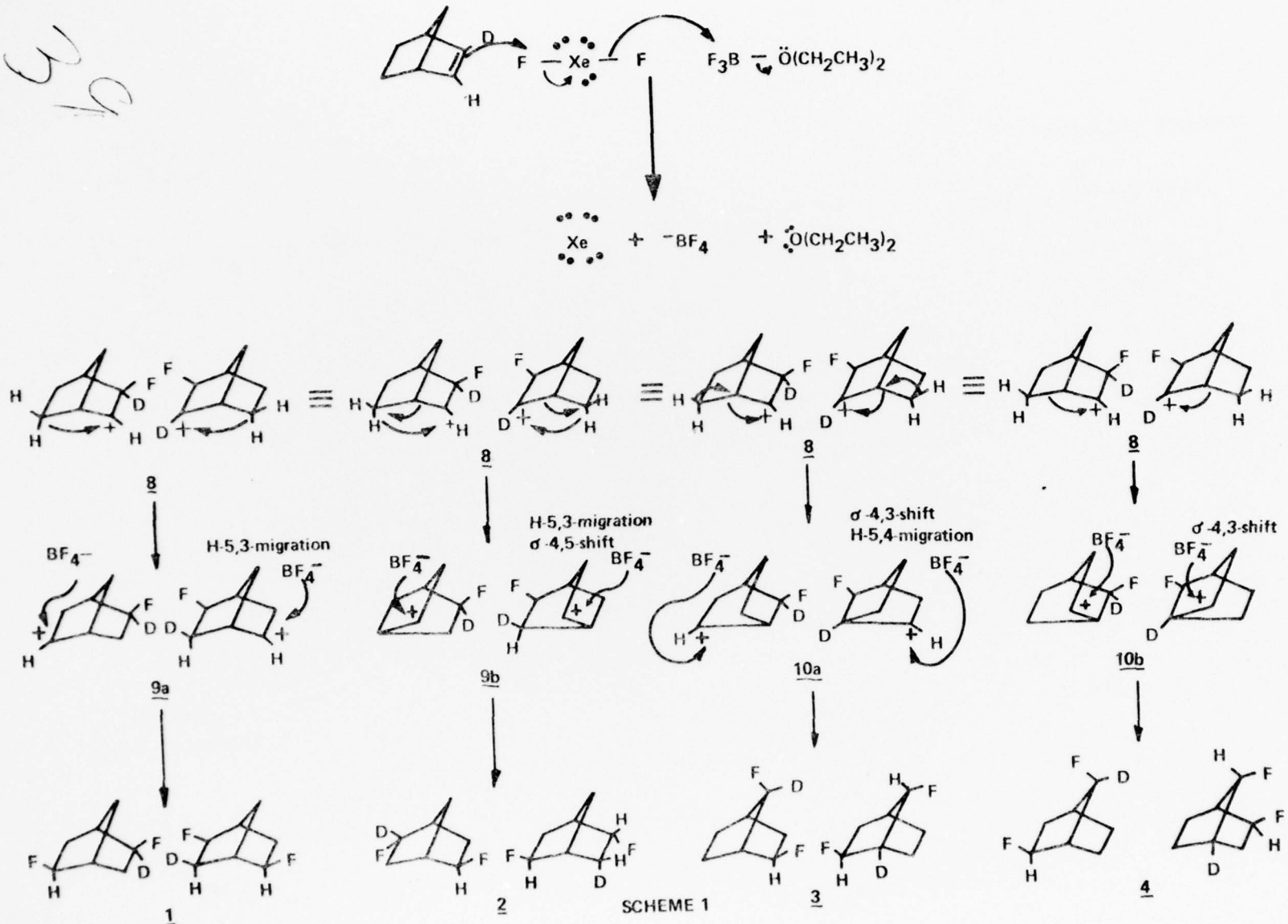
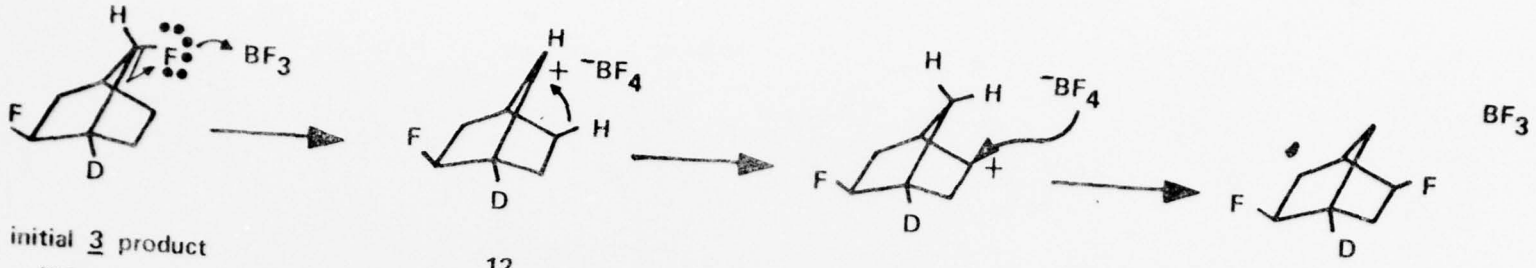
synthesize the 2-deuterionorbornene proved to be hazardous and quite unpredictable. In one case, the reaction was cooled too much (-78°C) while the n-butyl chloride was added dropwise to the stirred sodium metal suspension. At this cold temperature an immediate conversion to n-butyl sodium apparently did not occur causing a build-up of unreacted n-butyl chloride in the sodium metal suspension. Once reaction began, it quickly exothermed uncontrollably and exploded violently. Proper shielding and precautions should be instituted when attempting the described metalation reaction.


Xe
F
F3B
Ö(CH2CH3)2
−BF4
8
H-5,3-migration
σ-4,5-shift
σ-4,3-shift
H-5,4-migration
9a
9b
10a
10b
1
2
3
4

SCHEME 1



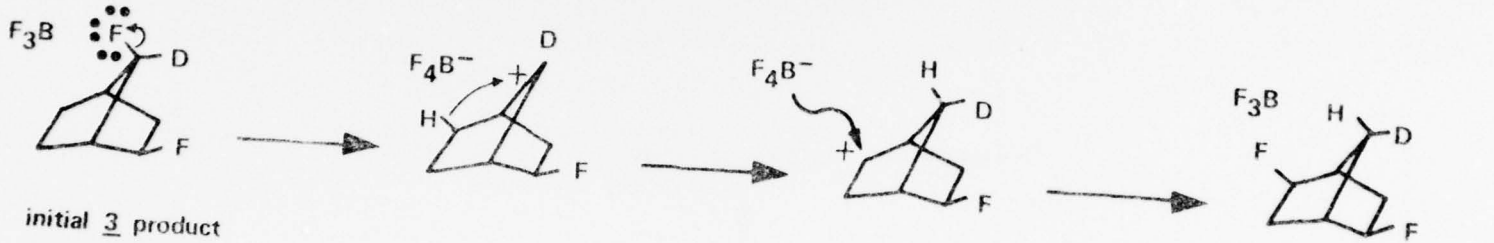
initial 3 product
(SCHEME 1)

12

9

isomerized 1 product

initial 1 products
(SCHEME 1)



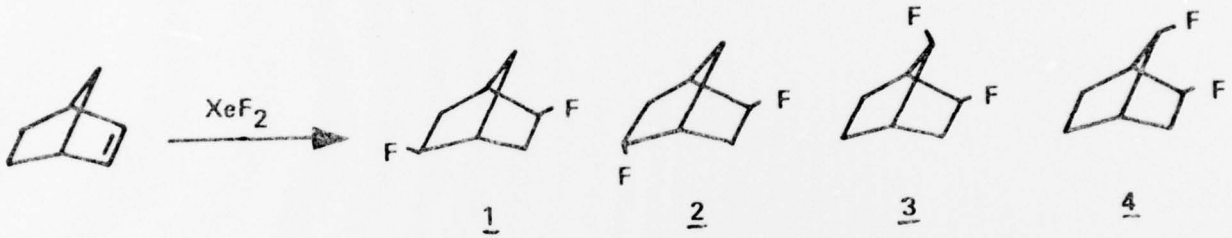
initial 3 product
(SCHEME 1)

12

9

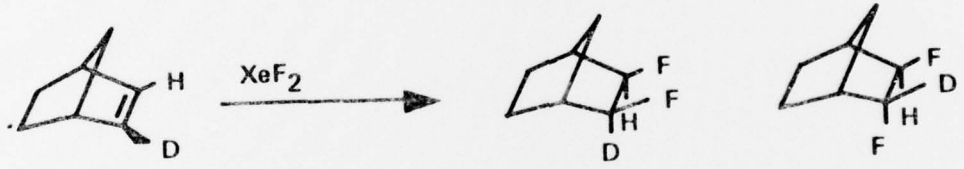
isomerized 1 product

SCHEME 2



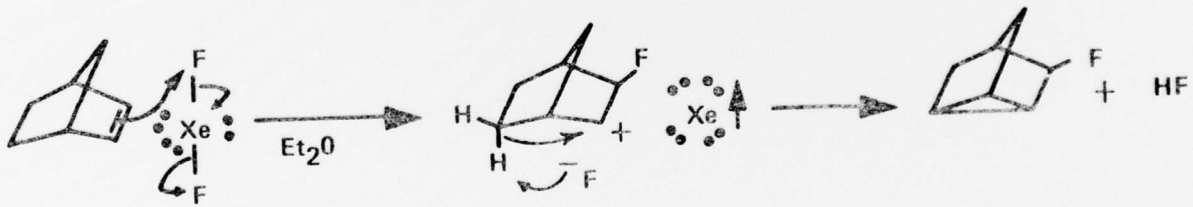
1 2 3 4 (1)

Equation 1



5 6 (2)

Equation 2



8 11 (3)

Equation 3